

# Quantitative Estimation of Fougerite Green Rust in Soils and Sediments by Citrate—Bicarbonate Kinetic Extractions

Frédéric Feder <sup>1,\*</sup>, Fabienne Trolard <sup>2,3</sup>, Guilhem Bourrié <sup>4</sup> and Goestar Klingelhöfer <sup>5</sup>

<sup>1</sup> CIRAD, UPR Recyclage et Risque, LMI IE SOL, BP 1386, 18 524 Dakar, Sénégal

<sup>2</sup> INRA, UMR 1114 Emmah, CS 40509, F-84914 Avignon CEDEX 9, France; fabienne.trolard@inra.fr

<sup>3</sup> UAPV, UMR 1114 Emmah, CS 40509, F-84914 Avignon CEDEX 9, France

<sup>4</sup> AAF, F75015 Paris, France; guilhem.bourrie@inra.fr

<sup>5</sup> Institut für Anorganische und Analytische Chemie, Johannes Gutenberg — Universität Mainz, Staudinger Weg 9, D-55099 Mainz, Germany; klingel@uni-mainz.de

\* Correspondence: frederic.feder@cirad.fr; Tel.: +33-4-6761-4944

Received: 15 August 2018; Accepted: 27 September 2018; Published: 1 October 2018

**Abstract:** Fougerite (IMA 203-057), from green rust (GR) group, is difficult to quantify due to its reactivity and its small concentration in soils and sediments. Chemical extractions with citrate-bicarbonate (CB) reagent, in kinetic mode, can be used for a pre-diagnosis. Performed by steps (0, 1, 6, 48, 168 and 504 h), the proposed protocol was applied on samples from Gleysol of Fougère’s forest with mineralogical controls by Mössbauer and XRD (X-ray diffraction) after each step of extraction. In less than 6 h, the first fraction extracted is composed of 70% Si, 80% Al, 23% Fe and 80% Mg of total element extractable by CB and is ascribed to the “indefinable mineral mixture Si-Al-Fe” named by Tamm. Between 6 and 168 h, the second fraction extracted is composed of Fe and Mg with a constant mole ratio Fe/Mg equal to 10 and is ascribed to the fougerite-GR phase. Analysis of XRD pattern and of Mössbauer spectra confirms: (i) all the other mineral phases containing Al, Mg, Si were not dissolved by CB after 6 h; (ii) the CB treatment extracts fougerite-GR completely. The residual fraction is composed of components not dissolved by CB extraction. Thus, the selectivity of CB can be used to quantitatively estimate the presence of fougerite-GRs in soils and sediments.

**Keywords:** green rust; fougerite; citrate-bicarbonate extraction; Mössbauer; iron; Fe; gley; hydromorphy

## 1. Introduction

In many environments, iron (Fe) minerals play a major role in biogeochemical cycles as electron donor and acceptor in oxidoreduction reactions. Soil genesis and properties are frequently influenced by Fe in soil solution and in minerals [1,2]. Many years ago, blue and green colors in reduced soils were associated with ferrous iron in solution and mixed Fe<sup>2+</sup> and Fe<sup>3+</sup> hydroxides, known as green rusts (GRs) [3–5]. They were suspected but unidentified in soils [6]. Natural GRs were recognized in soils for the first time by Trolard et al. [7,8] and fougerite, the natural GR, has been approved as a new mineral by the International Mineralogical Association (IMA) with the number 2003-057 [9]. Fougerite is a mixed M(II)-M(III) hydroxide of the GR group (or Layered Double Hydroxides LDH), where M(II) can be Fe or magnesium (Mg), and M(III) Fe. The general structural formula is [(Fe<sup>2+</sup>, Mg<sup>2+</sup>)<sub>1-x</sub> Fe<sup>3+</sup><sub>x</sub> (OH)<sub>2</sub>]<sup>x+</sup> [x/n A<sup>-n</sup>, mH<sub>2</sub>O]<sup>-</sup>, where  $x = \text{Fe}^{3+}/(\text{Fe} + \text{Mg})_{\text{tot}}$ , A is the interlayer anion and n its valency, with  $1/4 \leq x \leq 1/3$  and  $m \leq (1 - x)$ . The structure of GRs and parent minerals can accommodate a variety of anions, such as OH<sup>-</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> [9,10]. Iron control and equilibria between soil

solution and natural GRs were demonstrated in hydromorphic soils and constrain a narrow range of the GRs chemical composition [11,12].

Understanding the thermodynamic conditions of precipitation, equilibrium, and dissolution of natural or synthetic GRs is fundamental both to the current functioning of soils and sediments and to the genesis of iron-bearing geological formations. Under the geochemical and thermodynamic conditions prevailing in the oceans during the Precambrian era, GRs played a fundamental role in the genesis of iron formation [13] and even likely in the origin of life [14]. These geochemical conditions are similar to those currently being measured in reductive soils. The study of the thermodynamic equilibria between natural GRs and soil solution made it possible to establish a ternary solid solution model [10,15] taking into account the partial substitution of  $\text{Fe}^{2+}$  by  $\text{Mg}^{2+}$  [16]. There is a complex nexus of interactions between GRs, trace metals and metalloids. For example, GRs rapidly and completely reduce chromate ( $\text{Cr(VI)}$ ) into  $\text{Cr(III)}$  [17]. Conversely, aqueous  $\text{Fe(II)}$ , that can be released by GRs dissolution, can promote recrystallization of Cr-substituted goethites [18] with liberation of Cr in solution. In addition, the presence of certain metalloids such as arsenic (As) or antimony (Sb) [19] or changes in oxidation-reduction conditions [20] influence the precipitation or transformation of synthetic GRs.

GRs are unstable in air and transform easily by oxidation into  $\text{Fe}^{3+}$ -oxides (lepidocrocite, goethite); this transformation is accompanied by a color change of the sample from blue to ochre [1]. A special cell is necessary to keep the sample in nitrogen or argon atmosphere [7]. Thus, natural GRs are difficult to conserve, describe and analyze. XRD (X-ray diffraction) patterns, recorded on soils, fail to provide clear evidence about fougérite-GR mineral due to the diffuse and dilute nature of this mineral and the frequent presence of other dominant minerals such as kaolinite, whose diffraction peaks are very close to those of synthetic GRs, except with special data treatment with DECOMPXR software [15]. Chemical analyses of the whole soil could be performed but the natural mineral cannot be separated due to its labile character. Therefore, it is necessary to use more sensitive and specific techniques namely Mössbauer spectroscopy [7,8,12] or X-ray absorption spectroscopy at the Fe-K edge [16].

Beyond these strict mineralogical characterizations, some chemical methods have been developed to quantify specific reactive compartments after dissolution. Chemical extractions have been commonly used in soil science with this objective and the results used to compare soils from different origins [2,21]. Thus, several chemical reagents have been used to distinguish organic and/or mineral fractions and then to define diagnostic horizons and properties. Though these extractions are not specific of well-known mineralogical phases [1,22] they have been frequently used to define reference soil groups affected by different pedogeneses [23]. For example, organically bound Fe and aluminum (Al) can be extracted with a pyrophosphate solution. Free Fe, manganese (Mn) and Al in soils can be extracted using Dithionite-Citrate-Bicarbonate (DCB) reagent at high temperature, i.e., 60 °C [18] or at room temperature with a kinetic procedure [24–26]. Short-range-ordered or amorphous Fe, Al, and silica (Si) compounds are commonly extracted by an acid ammonium oxalate solution [27] particularly to refine XRD patterns on clay minerals [28] or by extraction by CB reagent [26] in alkaline conditions with the advantage that clay minerals are not dissolved. However, the procedure with ammonium oxalate cannot be used to dissolve GRs because oxalate anion can be incorporated in the structure to form a stable oxalate-GR [10]. Nevertheless, the CB reagent, i.e., DCB without the reductive contribution of dithionite, can be used to dissolve completely, in a few hours, synthetic GRs [7]. However to validate this procedure as a specific means of quantifying the amount of natural GR-fougérite in a soil sample, it is necessary to study the kinetics of elements released in solution associated with mineralogical controls step-by-step on the solid residue. This approach was used to define all the duration of common extraction procedure and sometimes to explain the association or the substitution of a specific element in some mineralogical phases [29,30].

Currently, there is no easily accessible method to identify GR, or to quantify the substitution of iron by magnesium. Therefore, this paper aims at assessing the selectivity of CB reagent to dissolve natural GRs and proposes a protocol to estimate their quantity present in soils or sediments by measurement of Fe and Mg dissolved with CB extractions. The adopted strategy is founded on: (i)

analyzing the Si, Al, Fe and Mg concentrations released by CB extraction as function of time and (ii) controlling by XRD and Mössbauer spectroscopy the evolution of mineral phases in the residue during these extractions.

## 2. Materials and Methods

### 2.1. Sampling Site

The soil profile studied is localized in the domanian forest (15 km<sup>2</sup>) at Fougères in Brittany, France (48°25' N, 1°10' W). Climatic conditions are oceanic, influenced by the Channel sea (50 km to the North) and the Atlantic Ocean. Vegetation is composed with oak and especially beech and minor species (holly, fern, nettle, and bramble). Altitude is 180 m above sea level at the bottom of a hill cut by numerous thalwegs into small watersheds, about 800 m long. The site is located near a spring, at about 200 m from the top of a hill. Soils are developed in a granitic saprolite (several meters thick) derived from the weathering of a granodiorite with cordierite. This saprolite is covered by two different silty formations. The deeper one is the result of in situ saprolite evolution and the second one is a loess deposition during the last glaciation (Weichselian), as evidenced by the discontinuities in grain size distribution at 30 and 70 cm depth (Table 1). The clay fraction, i.e., particle size < 2 µm, is maximum near 65 cm at the top of granitic saprolite. The profile chosen is situated in a soil catena made of Cambisols upslope and Gleysols downslope [21].

**Table 1.** pH<sub>water</sub>, pH<sub>KCl</sub>, carbon contents, total cation exchange capacity (CEC) and particle size distribution for the different horizons.

Depth <sup>1</sup> cm	pH <sub>water</sub>	pH <sub>KCl</sub>	C %	CEC cmol(+)·kg <sup>-1</sup>	CF <sup>a</sup> g·kg <sup>-1</sup>	FS <sup>a</sup> g·kg <sup>-1</sup>	CS <sup>a</sup> g·kg <sup>-1</sup>	S <sup>b</sup>
10 (OH/AG)	4.5	3.7	7.5	4.3	76	364.7	450.9	108.4
35 (Go)	4.5	3.7	1.6	1.7	109.6	262	536.5	91.9
65 (Gr)	4.8	3.7	0.5	4.5	167.8	206.3	453	172.9
75 (Gr)	4.2	3.4	0.4	4.9	119.5	185.3	278.9	416.3
85 (Cg)	5.2	4	0.7	5.2	118.8	197.4	150.1	533.7
95 (Cg)	4.8	3.7	0.4	6.1	98.6	182.8	131.4	587.3

<sup>1</sup> corresponding horizon in brackets (cf. description in text); <sup>a</sup> CF = Clay Fraction (<2 µm), FS = Fine Silt (2–20 µm), CS = Coarse Silt (20–50 µm) and S = Sand (50–2000 µm).

The soil profile is a Gleysol and the different horizons observed are:

- 0–15 cm (OH/AG): a black organic horizon above an organo-mineral horizon with a diffuse transition. No oxidoreduction mottles have been detected;
- 15–50 cm (Go): a silty horizon, with oximorphic properties, i.e., bluish-grey colors in cores (5 BG 6/1 according to Munsell's chart) with some discolorations along roots and numerous oxidoreduction mottles (specifically 5 Y 6/4 and 2.5 Y 5/6, moist); structure is massive and the piezometric level of the water table is frequently present in this horizon;
- 50–80 cm (Gr): a silty horizon, with reducing conditions, i.e., homogeneous in color and clearly blue (5 BG 6/1), almost permanently waterlogged (10 months per year), without roots. No oxidoreduction mottles have been observed. Texture changes progressively from 60 cm to 80 cm and limit between Gr and Cg is diffuse;
- 80 cm and more (Cg): the granitic saprolite with reducing properties, i.e., bluish-green color (5 BG 6/1), permanently waterlogged.

### 2.2. Soil Analysis

Total C of the initial soil was determined by dry combustion with an element analyzer (CHNS-O EA 1108, Carlo Erba Instrument). Cation exchange capacity (CEC) was measured by the

cobaltihexamine method at soil pH [31]. The pH water and pH KCl were measured according to the NF ISO 10390 standard at a soil/water volume ratio of 1:5 [21].

### 2.3. Soil Sampling

The soil sample was collected in the reductive horizon (Cg) in a large volume (a few dm<sup>3</sup>) with the surrounding soil solution and maintained under anoxic conditions in an airtight box without sieving or air-drying. All the manipulations of this soil sample were performed inside a glove box under N<sub>2</sub> atmosphere and with an oxygen trap. The permanence of the original blue or blue-green colors during all experiments is used as a preservation criterion.

### 2.4. Chemical Extraction Procedure with CB

In the glove box, 500 mg of soil sample were mixed in a polypropylene bottle with 50 mL of CB reagent. Soil/solution ratio is ca. 1 for 100 in weight. To prepare CB reagent, mix 9.82 g of sodium bicarbonate NaHCO<sub>3</sub> ( $M = 84 \text{ g}\cdot\text{mol}^{-1}$ ) with 78.43 g of tri-sodium-citrate Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> · 2 H<sub>2</sub>O ( $M = 294.1 \text{ g}\cdot\text{mol}^{-1}$ ) in 1 liter of ultra-pure water [30,32]. CB extractions were realized in separate bottles during 1, 6, 48, 168, 336 and 504 h with one repetition at each time of reaction. All samples were shaken three times a day. Extraction solutions were collected and filtered at 0.45 µm under N<sub>2</sub> atmosphere immediately with Millipore™ filters and then acidified with supra-pure HNO<sub>3</sub>. Analyses of Si, Al, Fe and Mg were quickly performed by inductively coupled plasma-atomic emission spectrometry (ICP-AES); the relative precision of measured concentrations ranges from 2% to 5%.

### 2.5. X-Ray Diffraction

XRD patterns were recorded on soil samples using a Siemens D5000 (40 kV, 20 mA) diffractometer with a graphite monochromator, Bragg-Brentano geometry, and Co-Kα1 radiation ( $\lambda = 1.7890 \text{ \AA}$ ). The dwell time in the 2–45° interval ( $2\theta$ ) was set to 1 s per 0.02° step (i.e., a total of about 1 h) on a rotating sample. The main crystalline phases (starting at a few percent) were indexed using Diffrac-AT software linked to the 1998 JCPDS database. Initial soil sample was also saturated with K, Mg and ethylene-glycol or heated to 350, 450 and 550 °C following the classical protocol to distinguish the main clay minerals [2,33]. XRD patterns were also recorded after 168 h of CB extraction on the initial soil sample. Collected after filtration under N<sub>2</sub> atmosphere inside the glove box, this treated sample was analyzed into an airtight cell specifically built up for this diffractometer. Then, this soil sample was heated at 550 °C and another XRD pattern was recorded.

### 2.6. Mössbauer Spectroscopy

As any Mössbauer spectrometer dedicated to iron, the instrument consists of (i) a source of 14.4 keV  $\gamma$ -ray, (ii) a drive generating by Doppler effect a variation of the incident wavelength, and (iii) detectors. Thus, Mössbauer spectrum is presented with the velocity of the source in mm·s<sup>-1</sup> in abscissa and the number of  $\gamma$ -rays emitted by the soil sample in ordinate. The instrument, initially designed for Mars missions requires high detection efficiency. Our Mössbauer spectrometer operates in backscattering geometry and not in classical transmission [34]. The comparison of spectra obtained by transmission or backscattering did not show any significant experimental differences [34]. Backscattering geometry is not influenced by the sample thickness. The main disadvantage is the secondary radiation caused by primary 122 keV radiations, for which an effective shielding of the detectors was designed. Si-PIN diodes were used as detectors, with efficiencies nearly 100% and 65% for 6.4 and 14.4 keV radiations, respectively. The velocity was calibrated with a 25 µm foil of  $\alpha$ -Fe at room temperature (RT) and the isomer shifts will thus be given with respect to this reference. The electron density at the nucleus determines the isomer shift  $\delta$ . Thus,  $\delta$  reflects specifically the oxidation states: Fe<sup>2+</sup> or Fe<sup>3+</sup>. The quadrupole splitting  $\Delta E_Q$  originates from non-uniform charge density and electric field gradient interactions with the iron nucleus.  $\Delta E_Q$  is influenced by the crystallinity, specifically by site distortion [1]. Our Mössbauer spectroscopy measurements were always done at RT. The Mössbauer spectra were fitted with Lorentzian functions. A set of free parameters was then

adjusted to minimize a goodness-of-fit criterion, the  $\chi^2$ . The free parameters are those that are only mutually bounded via the  $\chi^2$  minimization procedure. These parameters are the isomer shift  $\delta$ , the quadrupole splitting  $\Delta E_Q$ , the widths at half maximum and the height of the peaks, constrained to be equal for both lines of the doublet. The precision obtained on the  $x = \text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  ratio is better than the precision on each individual doublet, as errors partly compensate, and can be estimated as  $\pm 0.01$  by analyzing several samples several times. Quality of spectra depends essentially on iron concentration in the samples and duration of acquisition. The relative abundance of components is obtained by integration of the corresponding areas. Line intensities are directly proportional to the site abundance and vary from a mineral to another. Collected after filtration under  $\text{N}_2$  atmosphere inside the glove box, these residual solid soils were placed into an airtight cell specifically built up for this Mössbauer spectrometer. Mössbauer spectra were recorded after 6, 48, 168 and 504 h of CB extraction on the initial soil sample.

### 3. Results

The original blue-green color of samples was preserved during all experiments, which indicates that reductive conditions were maintained in the glove box. Oxidation of soil sample, i.e., transformation of fougérite-GR to lepidocrocite [1], would have been easily detected by the ochre coloration and the 6.26 Å peak on XRD patterns, that was not observed (*cf infra*).

#### 3.1. Kinetic Selective Extractions

Kinetic extraction of Si, Al, Fe and Mg by CB show different behaviors with time (Figure 1). Cumulative extracted fraction is expressed in percentage of the total absolute concentration of the element in the soil. Cumulated concentrations of Si extracted by CB were 1.3% after only 6 h and reached slowly 1.8% after 504 h (Table 2). Kinetic extraction of Al followed another pattern: Al extracted by CB increased quickly to 9.4% till 6 h and gradually until 48 h to reach 11.8% and remained constant till 504 h. Cumulated concentrations of Fe and Mg extracted by CB showed a pattern with three stages: at first, Fe and Mg concentrations in solution increased quickly respectively to 22.9% and 55.8%. During the second stage, between 8 and 168 h, Fe and Mg were released linearly till 97.1% and 69.1%, respectively until 168 h. Finally, Fe and Mg remained constant from 168 to 504 h.

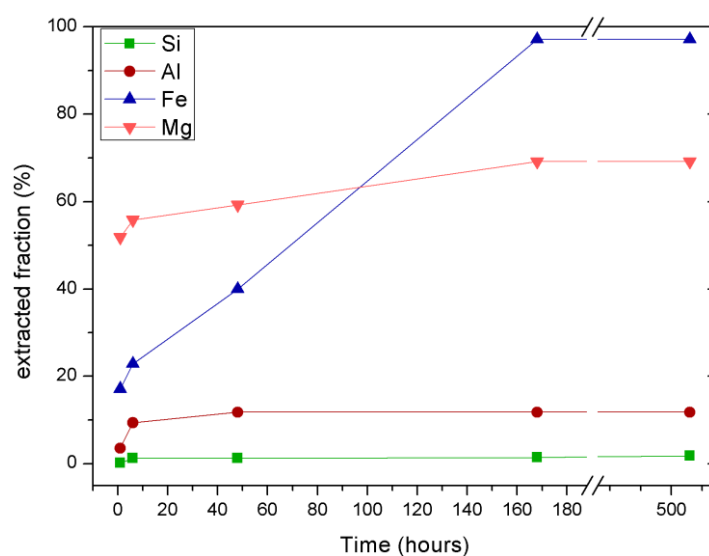


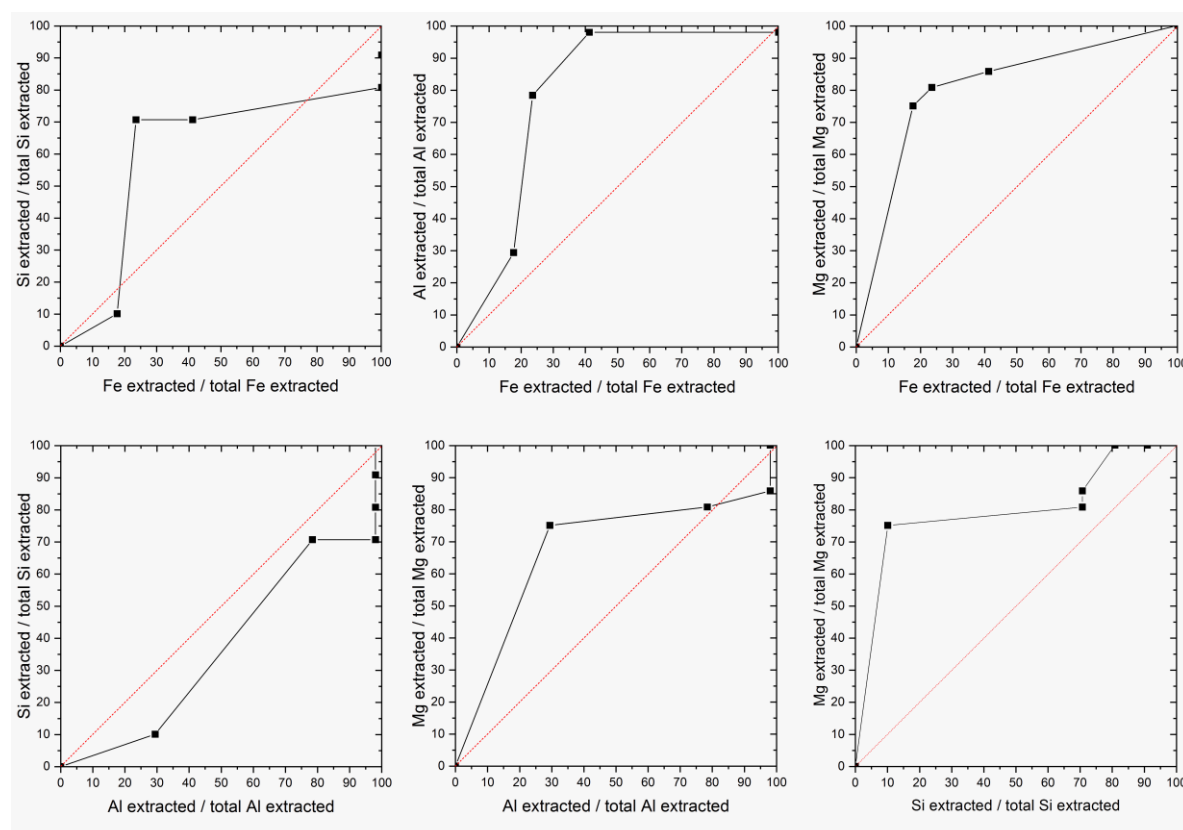
Figure 1. Kinetic extractions of Si, Al, Fe and Mg by citrate-bicarbonate.

**Table 2.** Total and exchangeable concentration of Si, Al, Fe and Mg in initial soil and after CB extractions as function of time.

		Si <sup>a</sup>	Al <sup>a</sup>	Fe <sup>a</sup>	Mg <sup>a</sup>
Initial soil	total	11,000	1700	700	405
	exchangeable	0	1	0.9	15.5
Time of CB	1	20	60	120	105
	6	140	160	160	226
Extraction (hours)	48	140	200	280	240
	168	160	200	680	280
	336	180	200	680	280
	504	200	200	680	280

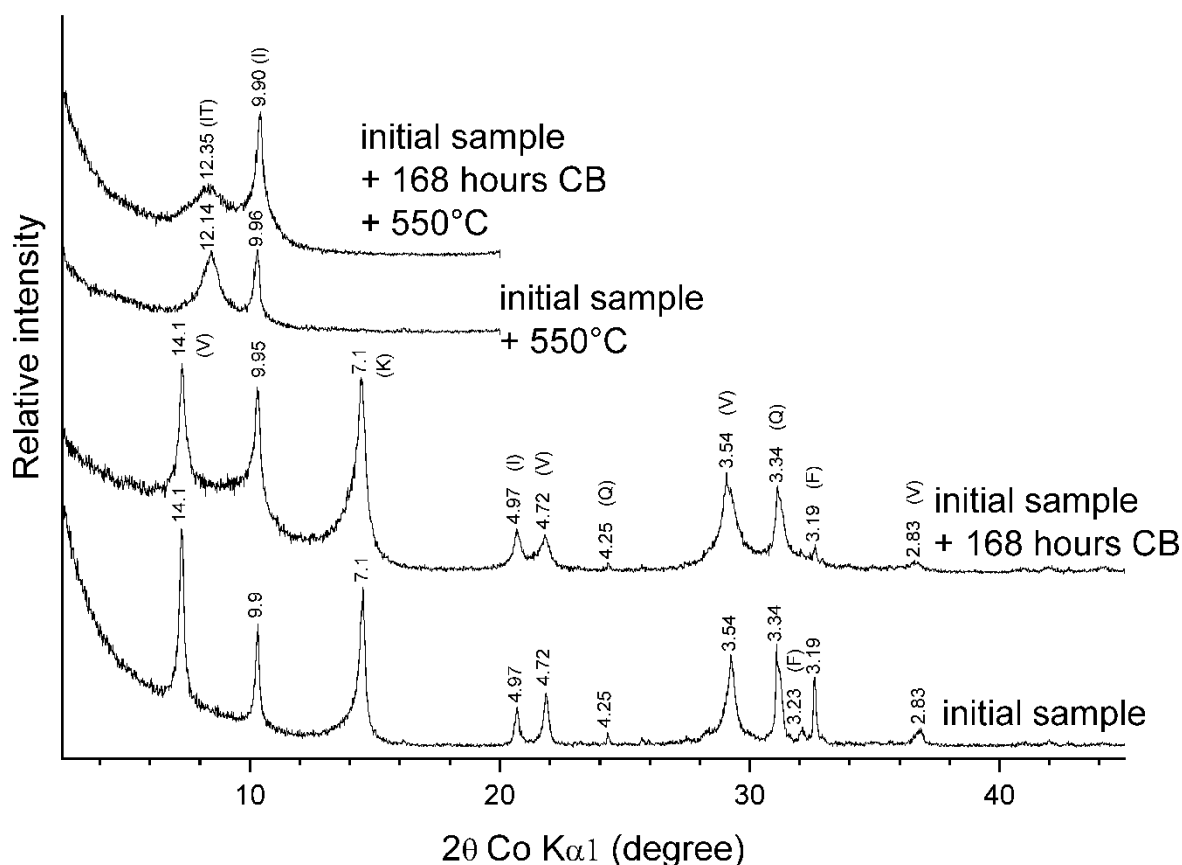
<sup>a</sup> expressed in mmol·kg<sup>-1</sup>.

Si, Al, Fe and Mg are present in different mineral phases dissolved separately by CB during time. Evidence for this is obtained by plotting the results of kinetic extractions of Si, Al, Fe and Mg versus each other (Figure 2) [30]. These elements never showed continuous and simple congruent dissolution. After 1 h of extraction by CB, the couples (Fe, Si), (Fe, Al) and (Al, Si) were close to the 1:1 bisector, corresponding to a congruent dissolution. Nevertheless, after 6 h, only the couple (Al, Si) was still close to the bisector. After 6 h, all couples of elements were far away from the bisector or crossed it at the end of the extraction by CB, which does not allow for an unequivocal interpretation of these extraction data. Only Mg was significantly present as exchangeable ions (Table 2) and is quickly released before iron phases.

**Figure 2.** Plots of the results of kinetic extractions by CB of Si, Al, Fe and Mg versus each other.

### 3.2. XRD Patterns

Even after 168 h of CB treatment, none of the main peaks of silicates were significantly affected. The raw diagrams, with the different treatments presented in material and methods, are shown in Figure 3.



**Figure 3.** From down to top, XRD patterns of initial soil sample, soil sample after 168 h of CB treatment and after heating at 550 °C of initial soil sample and after 168 h of CB treatment. Q = quartz, F = feldspar, K = kaolinite, I = illite, V = vermiculite, IT = intergraded mineral.

For the initial sample, quartz (Q: 3.34 Å), K-feldspar and plagioclase-feldspar (F: 3.23 and 3.19 Å) are identified. The 7.1 Å peak, which disappears after heating at 550 °C, is characteristic of kaolinite (K). The 9.94 Å peaks, that does not collapse with K saturation (raw diagram not shown), can be ascribed to illite (I). The 14.1 Å peak that does not collapse with K or ethylene-glycol saturation as with true vermiculites (V) but disappears on heating and shifts to 12.14 Å can be assigned to an intergraded mineral (IT) with some hydroxyl-ion interlayer because true chlorites would shift to 10 Å. After 6 h of CB extraction (not represented here), peak of interstratified minerals appears between 14.1 and 9.95 Å and persists unchanged until the end of the extractions (see XRD pattern of soil sample + 168 h CB). No iron oxide or oxy-hydroxide have been observed by XRD.

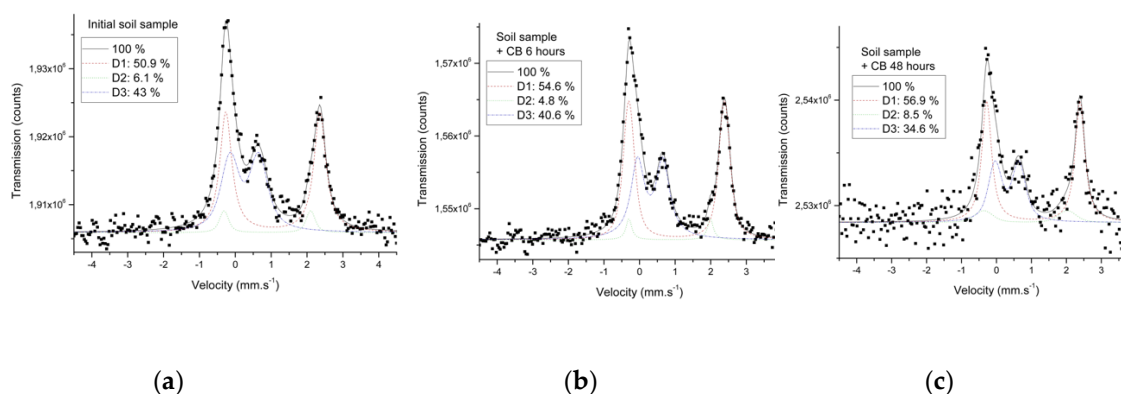
### 3.3. Mössbauer Spectra

Mössbauer spectra measured at RT with the computed hyperfine interaction parameters display the same characteristic quadrupole ferrous and ferric doublets as the fougierite obtained in situ [12]. Mössbauer spectrum of initial soil sample before CB treatment is given on Figure 4. Hyperfine interaction parameters obtained from computer fitting with Lorentzian-shape lines are given in Table 3. All the spectra had to be fitted with three quadrupole doublets. D1 and D2 correspond to ferrous ion sites and D3 correspond to ferric ion sites. According to the crystal structure of GR, the Mössbauer spectra of the compound were first fitted with only two doublets D1 and D3 for each crystal site. This

fit proved unsatisfactory and then the D2 doublet had to be added. These parameters correspond to the description of fougérite (IMA 2003-057) [9]. No other iron phases have been observed, the  $x = \text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  mole ratio was 0.43 and global spectrum quality was excellent.

**Table 3.** Hyperfine interaction parameters of Mössbauer spectra obtained at room temperature. D1, D2 and D3 are the three doublets (cf. Figure 4).  $\delta$  is the isomer shift (in  $\text{mm}\cdot\text{s}^{-1}$ ) with respect to the  $\alpha$ -Fe foil reference,  $\Delta E_Q$  is the quadrupole splitting (in  $\text{mm}\cdot\text{s}^{-1}$ ) and RA is the Relative Area of the components (in %).  $x = \text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  is equal to the relative area of D3 doublet; the estimation error on  $x$  is  $\pm 0.01$ .

Samples	D1			D2			D3		
	$\delta$	$\Delta E_Q$	RA	$\delta$	$\Delta E_Q$	RA	$\delta$	$\Delta E_Q$	RA
initial	1.05	2.62	50.9	0.89	2.41	6.1	0.25	0.80	43.0
+6 h CB	1.04	2.68	54.6	0.84	2.29	4.8	0.30	0.71	40.6
+48 h CB	1.05	2.67	56.9	0.83	2.39	8.5	0.30	0.68	34.6
+168 h CB	No spectrum								
+504 h CB	No spectrum								



**Figure 4.** Mössbauer spectra of soil samples: (a) initial; (b) after 6 h—CB extraction and (c) after 48 h—CB extraction.

#### 4. Discussion

In these selective extractions CB acts only as a single complexing agent in a medium, which is slightly alkaline (pH 7.8) by the buffering effect of sodium bicarbonate [32]. Thus, results show that three different compartments of reactivity can be distinguished by CB extractions as a function of time (Figure 1).

- The first fraction, F1, extractable for a duration less than 10 h, is composed of an “indefinable mixture” of Al, Si, Fe and Mg. During this step, 70% Si, 80% Al, 23% Fe and 80% Mg extractable by CB are released in solution.
- The second fraction, F2, extractable between 6 and 168 h, is essentially composed of Fe and Mg. During this time interval, 520  $\text{mmol kg}^{-1}$  of Fe and 54  $\text{mmol kg}^{-1}$  of Mg are released in solution with a constant mole ratio Fe/Mg equal to 10, whereas the Al and Si amounts are negligible.
- The third fraction, F3, is composed of the residual minerals, which are not dissolved by CB extraction.

The most labile mineral fraction F1 is very frequent in soils and, since 1922, Tamm proposed an extraction method based on the use of ammonium oxalate to remove it from solids, particularly from the clay fraction, and improve the quality of X-ray diagrams [28]. Tamm’s method is one of the methods of selective extraction commonly used in soil science (e.g., [1,22]), but it is less selective than CB extraction because it acts on the solid by a double mechanism: complexation by oxalate and acid dissolution at pH 4.5 [30].



Peak positions and intensities of the identified clay minerals (kaolinite, illite, vermiculite) were similar to those of the initial soil sample. Analysis of XRD pattern obtained after 168 h of CB treatment confirms that silicate minerals were not dissolved [35]. This previous result obtained by extraction with a buffered sodium dithionite solution on soil clays [35] was confirmed by extraction with a sodium-citrate solution on a dried and sieved soil sample from a nearby site [36]. Furthermore, cumulated concentration of Si extracted by CB treatment was very low and reached its maximum—1.3% of absolute total concentration in the soil—only after 6 h.

Al extracted by CB is a very small fraction of total Al (less than 2%); it can be assigned essentially to intergrade vermiculites. Ethylene-glycol saturation and displacement of the peak to 12.14 Å can be assigned to an intergrade mineral with some hydroxyl-ion interlayer as Al [33]. The presence of Al in the interlayers of vermiculites has been described long ago [37]. During this experimentation, Al was quickly extracted by CB: after just 6 h, ca. 75% of Al extractible after 504 h was reached and 100% after 48 h. This rate of Al extraction cannot be explained either by (i) the dissolution of silicate minerals because they are not dissolved; (ii) or by the dissolution of Al oxides because there is not any peak on XRD pattern [29]; (iii) or by the contribution of exchangeable Al because Al reached only 1 mmol<sub>(+)</sub>·kg<sup>-1</sup> soil significantly lower than the CB extracted concentration (Table 2). Thus, intergrade vermiculites are the major phases to explain these concentrations of extractable Al by the CB. In addition, for the 12.35 Å peak of the XRD patterns, the width at half height was broader and the height of the peak was twice less intense after the CB treatment and after the heating at 550 °C. These results are consistent with another study with soil samples from the same site [36]. The authors identified these minerals as intergrade vermiculite with hydroxyl-ion interlayer: Al (mainly) and Fe. They realized extraction with sodium-citrate and after the extraction of high amounts of Al, the mineral with 14 Å peak behaved as true vermiculite. They confirmed these results with another approach: the analysis of the thermodynamic equilibria between these minerals and the soil solution. This complex paragenesis is classical in acid brown soils (Luvisols, [21]) on granite under oceanic climate.

From 0 to 168 h, CB extracted more than 97% of total Fe in the soil and then fougérite-GR could not be identified by Mössbauer spectroscopy. CB extraction of Fe showed two main stages. The first one, from 0 to 6 h, corresponds to the fougérite-GR phases extractible with CB and the iron minerals easily extractible by CB with the same kinetics than Al or Mg in intergrade mineral or easily extractible iron phases [29]. Al, mainly, and Fe were both present as some hydroxyl-ions in the interlayer of intergrade minerals and Al and Fe could be simultaneously extracted from intergrade minerals by successive citrate extractions [36]. The second stage occurred from 6 to 168 h and corresponds mainly to the fougérite-GR phase extractible with CB because all the other mineral phases containing Al, Mg, Si were not dissolved by CB after 6 h.

For Mössbauer results, in the initial soil sample,  $x$  ratio was 43% and after kinetic extraction by CB decreased continuously until 34.6% after 48 h. These values of  $x$  ratio are consistent with the field observation: from 0.34 to 0.64 [12].

Global quality of Mössbauer spectrum was still good after 6 h of CB treatment (Figure 4); but after 48 h of the CB extraction, peak intensities were smaller and differences between the experimental data and the computed curve were larger for this spectrum. A smaller amount of fougérite-GR could explain this spectrum quality. We have a confirmation of this trend with the total absence of Mössbauer spectrum (not shown) after 168 and 504 h of CB extraction (Table 3). This result is consistent with the first evidence of CB selectivity to dissolve synthetic GR [7].

The concentrations of Mg extracted by CB were close to the maximum values after 6 h of CB treatment. Mg originates mainly from fougérite-GR. Figure 2 shows that both Fe and Mg are released congruently between 6 h and 154 h of extraction. Thus, the Mg proportion in fougérite-GR can be quantified from CB extraction and estimated to 10%. Relative differences between extracted amounts of Mg after 6 h and maximal values were close to 5%. This confirms the partial substitution of Fe<sup>2+</sup> by Mg<sup>2+</sup> in fougérite observed by EXAFS and XANES [16].

## 5. Conclusions

Oxidoreduction processes couple biogeochemical cycles of Fe and many elements. Fougerite is a major ferrous component of soils and sediments, and interacts with many major (Mg, N, S), minor or trace elements, both metals (Cu, Hg, Ag, Au) and metalloids (Se, As, Sb). Its large reactivity involves abiotic and biotic processes. Extraction by CB in a kinetic mode can be used to establish a pre-diagnosis of occurrence of fougerite-GR mineral in soils and allows for quantifying it, especially in reductive environments. The procedure can be transposed to sediments. The disappearance of fougerite-GR, attested by Mössbauer spectroscopy, and the dynamics of Fe and Mg extraction by CB in kinetic mode prove the selectivity of CB procedure to dissolve fougerite-GR. The proposed protocol is given in Annex A. It is easier and cheaper than sophisticated spectroscopies, and well suited for soil survey studies. It allows for a first characterization and selection of samples for further studies e.g., by Mössbauer spectroscopy. In addition, analysis of elements released correlatively with Fe allows for identification of elements associated with fougerite by substitution or adsorbed on soil solid components.

**Author Contributions:** T.F., F.F. and K.G. conceived and designed the experiments; F.F. and K.G., performed the experiments; F.F., T.F., B.G. and K.G. analyzed the data; K.G. contributed to Mössbauer facilities at Darmstadt University; F.F., T.F. and B.G. wrote the paper.

**Funding:** This research was funded by INRA (post-doctoral grant of G. Klingelhöfer), by the French “Programme National de Recherche Sol et Erosion” (PNSE) and by the Ministère de la Recherche (pre-doctoral grant F. Feder) .

**Acknowledgments:** Klingelhöfer G. acknowledges the support of the University Darmstadt, Germany, and the Germany Space Agency DLR, Bonn, Germany.

**Conflicts of Interest:** The authors declare no conflict of interest.

## Appendix A

Protocol for extraction of fougerite GR with CB reagent.

### Appendix A.1. Soil Sample

The soil sample must be collected in a large volume (a few dm<sup>3</sup>) with the surrounding soil solution if present and maintained under anoxic conditions in an airtight box without sieving or air-drying. All the manipulations of this soil sample must be performed inside a glove box under nitrogen atmosphere and with an oxygen trap.

### Appendix A.2. Reagent

Preparation of CB reagent: mix 9.82 g of sodium bicarbonate NaHCO<sub>3</sub> (M = 84 g·mol<sup>-1</sup>) with 78.43 g of tri-sodium-citrate Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> · 2 H<sub>2</sub>O (M = 294.1 g·mol<sup>-1</sup>) in 1 liter of ultra-pure water. Store in a bottle covered in foil.

### Appendix A.3. Procedure

- (1). In a glove box in darkness, weigh, in 12 separate 50 mL tubes, 500 mg of soil sample. One or two repetitions at each time of reaction.
- (2). Add 50 mL of CB reagent to each tube. Soil/solution ratio is ca. 1 for 100 in weight.
- (3). Close tubes and shake on high for 10 min.
- (4). After 1 h, shake and collect supernatant solutions.
- (5). Immediately, filter at 0.45 µm with Millipore filters.
- (6). Acidify with supra-pure HNO<sub>3</sub>.
- (7). Repeat operation from points 4 to 6 for extraction after 6, 48, 168, 336 and 504 h.
- (8). Shake all samples three times a day.

- (9). Quickly perform analyses of Si, Al, Fe and Mg by inductively coupled plasma-atomic emission spectrometry (ICP-AES).
- (10). Compute the % of each element extracted relative to the total concentration of the element and plot the % of extraction vs. time (see Figure 1).

Warning: To obtain to the same day the supernatant solutions for analysis by (ICP-AES), plan the time of duration of extraction inversely to the collection of supernatant solutions.

#### Appendix A.4. Method of Interpretation

For the calculation we used here the experimental data given in this paper as example. The quantity of Fe extracted from fougérite is given by the difference between the number of millimol/kg at the plateau and the intercept of the straight line with the vertical axis (see Figure 1), e.g., (see Table 2):  $[\text{Fe}(168 \text{ h})] - [\text{Fe}(48 \text{ h})] = 680 - 280 = 400 \text{ millimol/kg}$ . This amounts to 57% of total Fe in the soil (400/700). The quantity of Mg extracted from fougérite is obtained in the same way as:  $[\text{Mg}(168 \text{ h})] - [\text{Mg}(48 \text{ h})] = 280 - 240 = 40 \text{ millimol/kg}$ . Accordingly, Mg substitution for Fe amounts to 10%.

The structural formula of fougérite can only be calculated if the ratio  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$  is known, from Mössbauer spectroscopy. It is 43% in our sample (Table 3). Then the structural formula obtained is  $[(\text{Fe}^{2+}_{0.51} \text{Mg}^{2+}_{0.09}) \text{Fe}^{3+}_{0.40} (\text{OH})_2]^{0.4+} [0.4 \text{A}^-, \text{mH}_2\text{O}]^{0.4-}$ , where  $\text{A}^-$  the interlayered anion in fougérite, which cannot be determined by this method.

#### References

1. Cornell, R.M.; Schwermann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*; John Wiley & Sons: New York, NY, USA, 2003.
2. Soil Survey Staff. *Keys to Soil Taxonomy*, 12th ed.; USDA-Natural Resources Conservation Service: Washington, DC, USA, 2014.
3. Vysotskii, G.N. Gley. *Pochvovedeniye* **1905**, *4*, 291–327.
4. Vysotskii, G.N. Gley. An abridged publication of Vysotskii 1905 on the 257th Anniversary of the Russian Academy of Science. *Eurasian Soil Sci. J.* **1999**, *32*, 1063–1068.
5. Ponnamperna, F.N.; Tianco, E.M.; Loy, T. Redox equilibria in flooded soils: I. The iron hydroxide systems. *Soil Sci. J.* **1967**, *103*, 374–382.
6. Bernal, J.D.; Dasgupta, D.R.; Mackay, A.L. The Oxides and Hydroxides of Iron and Their Structural Inter-Relationships. *Clay Miner. Bull.* **1959**, *4*, 15–21.
7. Trolard, F.; Abdelmoula, M.; Bourrié, G.; Humbert, B.; Génin, J.-M.R. Mise en évidence d'un constituant de type "rouilles vertes" dans les sols hydromorphes—Proposition de l'existence d'un nouveau minéral: La "fougérite". *CR Acad. Sci.* **1996**, *323*, 1015–1022.
8. Trolard, F.; Génin, J.-M.R.; Abdelmoula, M.; Bourrié, G.; Humbert, B.; Herbillon, A.J. Identification of a green rust mineral in a reductomorphic soil by Mössbauer and Raman spectroscopies. *Geochim. Cosmochim. Acta* **1997**, *61*, 1107–1111.
9. Trolard, F.; Bourrié, G.; Abdelmoula, M.; Refait, P.H.; Feder, F. Fougérite, a new mineral of the pyroaurite-iowaite group: Description and crystal structure. *Clays Clay Miner.* **2007**, *55*, 323–334.
10. Bourrié, G.; Trolard, F.; Refait, P.H.; Feder, F. A solid-solution model for Fe(II)-Fe(III)-Mg(II) green rusts and fougérite and estimation of their Gibbs free energies of formation. *Clays Clay Miner.* **2004**, *52*, 382–394.
11. Bourrié, G.; Trolard, F.; Génin, J.-M.R.; Jaffrezic, A.; Maître, V.; Abdelmoula, M. Iron control by equilibria between hydroxy-green rusts and solutions in hydromorphic soils. *Geochim. Cosmochim. Acta* **1999**, *63*, 3417–3427.
12. Feder, F.; Trolard, F.; Klingelhöfer, G.; Bourrié, G. In situ Mössbauer spectroscopy: Evidence for green rust (fougérite) in a gleysol and its mineralogical transformations with time and depth. *Geochim. Cosmochim. Acta* **2005**, *69*, 4463–4483.
13. Halevy, I.; Alesker, M.; Schuster, E.M.; Popovitz-Biro, R.; Feldman, Y. A Key Role for Green Rust in the Precambrian Oceans and the Genesis of Iron Formations. *Nat. Geosci.* **2017**, *10*, 135–139.
14. Russell, M. Green rust: The simple organizing "seed" of all life. *Life* **2018**, *8*, 35.
15. Trolard, F.; Bourrié, G. Chapter 5: Geochemistry of Green Rusts and Fougérite. *Adv. Agronomy* **2008**, *99*, 227–288.

16. Refait, P.H.; Abdelmoula, M.; Trolard, F.; Génin, J.-M.R.; Ehrhardt, J.J.; Bourrié, G. Mössbauer and XAS study of a green rust mineral; the partial substitution of  $\text{Fe}^{2+}$  by  $\text{Mg}^{2+}$ . *Amer. Mineralogist* **2001**, *86*, 731–739.
17. Loyaux-Lawniczak, S.; Refait, P.; Ehrhardt, J.J.; Lecomte, P.; Génin, J.M.R. The reduction of chromate ions by Fe(II) layered hydroxides. *Hydrol. Earth Syst. Sci.* **1999**, *3*, 593–599.
18. Hua, J.; Chen, M.; Liu, C.; Li, F.; Long, J.; Gao, T.; Wu, F.; Lei, J.; Gu, M. Cr release from Cr-substituted goethite during aqueous Fe(II) induced recrystallization. *Minerals* **2018**, *8*, 367.
19. Karimian, N.; Johnston, S.G.; Burton, E.D. Antimony and Arsenic Behavior during Fe(II)-Induced Transformation of Jarosite. *Environ. Sci. Technol.* **2017**, *51*, 4259–4268.
20. Jones, A.; Cassandra, M.; Murphy, A.; Waite, T.D.; Collins, R.N. Fe(II) Interactions with Smectites: Temporal Changes in Redox Reactivity and the Formation of Green Rust. *Environ. Sci. Technol.* **2017**, *51*, 12573–12582.
21. IUSS Working Group WRB. *World Reference base for Soil Resources 2014. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*; World Soil Resources; Reports No. 106; Food and Agriculture Organization: Rome, Italy, 2014.
22. Borggaard, O.K. Phase identification by selective dissolution techniques. In *Iron in Soils and Clay Minerals*, Stucki, D., Ed.; Reibel Publishing Compagny: Dordrecht, The Netherlands, 1988; pp. 83–98.
23. Feder, F. Soil map update: Procedure and problems encountered for the island of Réunion. *Catena* **2013**, *110*, 215–224.
24. Mehra, O.P.; Jackson, M.L. Iron oxides removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* **1960**, *7*, 317–327.
25. Tessier, A.; Campbell, P.G.C.; Bisson, M. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Anal. Chem.* **1979**, *51*, 844–851.
26. Jeanroy, E.; Guillet, B.; Delcroix, P.; Janot, Ch. Les formes du fer dans les sols : Confrontation des méthodes chimiques avec la spectrométrie Mössbauer. *Sci. Sol.* **1983**, *3–4*, 185–194.
27. Alary, K.; Babre, D.; Caner, L.; Feder, F.; Szwarc, M.; Naudan, M.; Bourgeon, G. Pre-treatment of soil samples rich in short-range-order minerals before particle-size analysis by the pipette method. *Pedosphere* **2013**, *23*, 20–28.
28. Tamm, O. Eine Method zur Bestimmung der organischen Komponenten des Gelcomplexes in Boden. *Medd. Statens Skogsförsöksanstalt* **1922**, *19*, 385–404.
29. Singh, B., and Gilkes, R.J. Properties and Distribution of Iron Oxides and Their Association with Minor Elements in the Soils of South-Western Australia. *J. Soil Sci.* **1992**, *43*, 77–98.
30. Trolard, F.; Bourrié, G.; Jeanroy, E.; Herbillon, A.J.; Martin, H. Trace metals in natural iron oxides from laterites: A study using selective kinetic extraction. *Geochim. Cosmochim. Acta* **1995**, *59*, 1285–1297.
31. Ciesielski, H.; Sterckeman, T.; Santerne, M.; Willery, J.-P. Determination of cation exchange capacity and exchangeable cations in soils by means of cobalt hexamine trichloride. Effects of experimental conditions. *Agronomie* **1997**, *17*, 1–7.
32. Jeanroy, E.; Rajot, J.L.; Pilon, P.; Herbillon, A.J. Differential dissolution of hematite and goethite in dithionite and its application on soil yellowing. *Geoderma* **1991**, *50*, 79–94.
33. Righi, D.; Girault, P.; Meunier, A. Transformation des phyllosilicates dans un sol cryptopodzolique humifère du plateau de Millevaches, France. *Clay Miner.* **1986**, *21*, 43–54.
34. Klingelhöfer, G.; Morris, R.V.; Bernhardt, B.; Rodionov, D.; de Souza, P.A.; Squyres, S.W.; Foh, J.; Kankeleit, E.; Bonnes, U.; et al. Athena MIMOS II Mössbauer spectrometer investigation. *J. Geophys. Res.* **2003**, *108*, 8067–8082.
35. Mitchell, B.D.; Smith, B.F.L.; Endredy, A.S. The effect of buffered sodium dithionite solution and ultrasonic agitation on soil clays. *Israelian J. Chem.* **1971**, *9*, 45–52.
36. Aourousseau, P.; Curmi, P.; Bouillé, S.; Charpentier, S. Les vermiculites hydroxy-alumineuses du massif Armoricaïn (France). Approches minéralogique, microanalytique et thermodynamique. *Geoderma* **1983**, *31*, 17–40.
37. Farmer, V.C.; Smith, B.F.L.; Wilson, M.J.; Loveland, P.J.; Payton, R. W. Readily-Extractable Hydroxyaluminium Interlayers in Clay-and Silt-Sized Vermiculite. *Clay Miner.* **1988**, *23*, 271–277.

